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Thermal stability of poly(trimethylene terephthalate)

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Abstract

The first-order thermal degradation rates of poly(trimethylene terephthalate) [PTT] at 240–280 °C under non-oxidative conditions have been determined from the increase in allyl endgroups (^{1}H NMR) which closely match the rates determined from the decrease in molecular weight (intrinsic viscosity). Consequently, the predominant thermal degradation mechanism of PTT is consistent with concerted, electrocyclic oxo retro-ene chain cleavage under conditions pertinent to viable polymerization processes and efficient downstream extrusion and spinning into fiber. Although catalysts, additives and other reaction variables can influence the thermo-oxidative stability of polyesters including PTT, these factors have been found to have little or no effect on PTT thermal degradation rates under non-oxidative environments. The thermal stability of poly(butylene terephthalate) [PBT] has also been determined from butenyl endgroups (NMR) and molecular weight (IV). The activation energies (E_a) for both PTT and PBT thermal chain cleavage are similar to the reported E_as for poly(ethylene terephthalate) [PET] degradation, which is further supported by semi-empirical molecular orbital calculations on model compounds. However, both PTT and PBT undergo molecular weight decrease faster than PET. The apparent slower chain cleavage of PET is attributed to the contribution of productive chain propagation reactions due to unstable vinyl endgroups which alters the equilibrium stoichiometry compared to the relatively stable endgroups of PTT and PBT.

Keywords: Poly(trimethylene terephthalate); Thermal degradation rate; Polyester stability

1. Introduction

Poly(trimethylene terephthalate) [PTT] was reported over fifty years ago by Whinfield and Dickson [1] and exhibits exceptional properties, such as excellent elastic recovery [2] and inherent stain resistance. However, PTT was not commercialized until the late 1990s when Shell Chemical LP developed a route to 1,3-propanediol (PDO) monomer by hydroformylation of ethylene oxide [3]. Consequently, few studies of the thermal stability of PTT have been reported [4] and none under conditions pertinent to the polymerization reaction, viz. <280 °C under inert atmosphere. Thermal degradation, here defined as the decrease in molecular weight as a function of temperature, occurs simultaneously with chain propagation, so understanding and quantifying PTT thermal stability is important for developing viable polymerization processes [5] and also pertinent to efficient extrusion into fibers [6].

We report the first measurements of the thermal degradation kinetics and activation energies for PTT at 240–280 °C by following both the increase of allyl endgroups by ^{1}H NMR and the decrease in molecular weight by intrinsic viscosity (IV). The effects of catalysts, additives and process variations on thermal stability have been examined. The kinetics of poly(butylene terephthalate) [PBT] thermal degradation also have been measured under similar conditions by following the formation of butenyl endgroups and by IV. Comparisons to the thermal degradation of poly(ethylene terephthalate) [PET] suggest that the chemistry of the endgroups formed by thermal chain cleavage have important consequences on the observed apparent thermal stabilities of these polyesters.

2. Experimental

2.1. Materials

The control PTT was Shell commercial grade Corterra®

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polymer SH101 (IV = 0.92 dL/g; mp ~ 227 °C) made by solid-state polymerization (SSP) containing ~ 40–60 ppm Ti catalyst, a small amount of hindered phenol stabilizer [25] and no cobalt acetate toner or TiO_2 delustering agent. Some SSP samples were prepared in pilot scale equipment [25]. The very low or 'no catalyst' PTT sample was made without any added catalyst, which resulted in exceptionally long polymerization times. X-ray fluorescence indicated ~ 3 ppm residual Ti in this sample compared to 40 ppm or more Ti for the other PTT compositions. The 'all-melt' samples were prepared from terephthalic acid (TPA) or dimethyl terephthalate (DMT) processes, as previously described [5]. All SSP samples contained about 2.4–3.0 mol% linear dipropylene glycol [DPG] comonomer units, which is a consequence of in situ dimerization of PDO during polymerization [5,25]. PTT from the all-melt or DMT processes contained lower DPG levels (Table 2). All samples were in the form of pellets (chips). Except as noted, the initial IV was 0.91–0.94 dL/g.

PTT cyclic dimer (CAS number 254974-92-0) was collected from batch solid state polymerizations and recrystallized from tetrahydrofuran to give bright needles > 99.9% purity by NMR.

PET was a commercial sample (Shell) made with antimony catalyst, IV = 0.83 measured in 60/40 phenol/tetrachloroethane. PBT was a commercial sample made with titanium catalyst; IV = 1.27 measured in hexafluoroisopropanol.

2.2. General procedure

Typically, five glass tubes were charged with 1–5 g polymer each and dried in a vacuum oven with nitrogen bleed at 130 °C overnight. Control runs showed that this drying procedure was more effective than typical procedures used for fiber production. The hot tubes were connected via ground glass joints and flexible tubing to a manifold connected to purified nitrogen and vacuum using a Firestone™ valve and the tubes were degassed at least three times. Except as noted, the reaction was conducted under 1 atm (absolute) purified nitrogen. For some experiments, as noted, the reaction was conducted under full vacuum at < 2 mbar. The tubes were immersed simultaneously into a stirred silicon oil bath controlled to within 1 °C at the desired temperature (240–290 °C) and degassed again before the first sample was removed after 10 min. Subsequent samples were usually removed after 1, 2, 4, and 6 h after the first sample. The tubes were quickly cooled and the entire sample was ground for analyses. PTT experiments were conducted at 240, 260, 270 and 280 °C; PBT at 260, 270 and 280 °C; and PET at 270, 280 and 290 °C. For the side-by-side experiment, the control and 'no catalyst' samples were placed in the same oil bath and removed at the same times.

Intrinsic viscosity (IV) for PTT was measured in hexafluoroisopropanol and converted by established correlation to the corresponding IV values for 60/40 phenol/tetrachloroethane solvent at 30 °C with an estimated precision of ±0.01 IV units for measurements on duplicate samples.

2.3. NMR analysis

Allyl endgroups and butenyl endgroups were determined by proton NMR using a Varian Inova-500 spectrometer with ~ 40 mg polymer dissolved in 1 mL 50/50 v/v deuterated trifluoroacetic acid and $CDCl_3$ using a standard 30° tip pulse-and-acquire sequence (8 KHz spectral width, 64 K buffer, 5 s delay, 64 scans). The allyl endgroup proton peaks at 5.40–5.48 and 5.33–5.40 ppm relative to Me_4Si standard were used to calculate mol% based on total allyl, dipropylene glycol (DPG) and 1,3-propanediol (PDO) units. Similarly, the butenyl endgroup protons at 5.08–5.25 and 2.52–2.64 ppm were used to determine mol% based on total butenyl, dibutylene glycol, and 1,4-butanediol units.

2.4. Kinetic analyses

The mol% of allyl (or butenyl) endgroups was used to calculate disappearance of PDO (or BDO) units for first-order plots of $\mathrm{Ln}(PDO/PDO_0)$, where PDO_0 is the initial fraction of PDO units. The actual molar concentration (moles/liter) of PDO units would require a correction for the melt density at the reaction temperatures, which is not known accurately. However, because the rate constants for first-order kinetics are units of time^{-1}, the rate constants are experimentally relevant.

In the case of the small series of experiments with lower DPG comonomer content (entries 10–13, Table 2), the first-order rate constants based on molecular weight are not reported because of insufficient IV data. However, the IV changes for these four samples over the first hour at 270 °C were measured, as follows (initial IV, 1 h IV): 0.91, 0.60 (3 mol% DPG); 0.90, 0.56 (1.6%); 0.90, 0.58 (0.4%); 0.91, 0.59 (0.2%). The decrease in each case is within experimental error of the average decrease of 0.32 ± 0.02 IV units, which covers the practical M_w range of interest.

The data for PBT experiments (not shown graphically) at initial, 0, 1, 2, 4, and 6 h were IV (dL/g): 1.27, 1.22, 1.01, 0.82, 0.59, 0.52 (260 °C); 1.27, 1.19, 0.77, 0.63, 0.49, 0.35 (270 °C); 1.27, 1.11, 0.55, 0.39, 0.26, 0.21 (280 °C); Butenyl endgroups (mol%): 0.1, 0.2, 0.5, 0.9, 1.7, 2.2 (260 °C); 0.1, 0.2, 0.9, 1.3, 2.2, 3.6 (270 °C); 0.1, 0.4, 2.0, 3.2, 5.7, 7.2 (280 °C).

2.5. Semi-empirical molecular orbital calculations

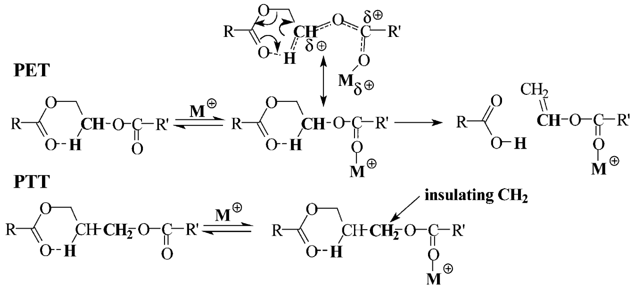
Calculations were performed using the ChemCAChe (version 3.8) suit of programs (CAChe Group of Fujitsu) on an IBM RS6000 with a Macintosh interface. The initial model reaction was ethyl formate to ethylene and formic acid. The energies of the reactant, transition state and products of the initial model were optimized using the MOPAC PM3 semi-empirical MO method. The 'intrinsic reaction coordinate' function confirmed that the transition state led to the proper starting and final products. The calculated transition state was confirmed to have one negative eigenvector and one associated imaginary vibration at $-1330\ \mathrm{cm}^{-1}$. The structures of the reactants, products and transition states were built up in incremental steps, which facilitated re-optimization at each stage. Twenty-eight reactions were calculated, culminating with the bis(methylterephthalate) esters of EG, PDO and BDO (Table 4). The single, imaginary vibrations of the transition states of the terephthalates were generally in the range of -900 to $-1000\ \mathrm{cm}^{-1}$. Free energies ΔG based on the PM3 method for loss of vinyl and allyl endgroups by transesterification as acetaldehyde and allyl alcohol, respectively, were calculated at 300–600 K and the reaction ΔG at 550 K (277 °C) is shown in Table 5.

3. Results and discussion

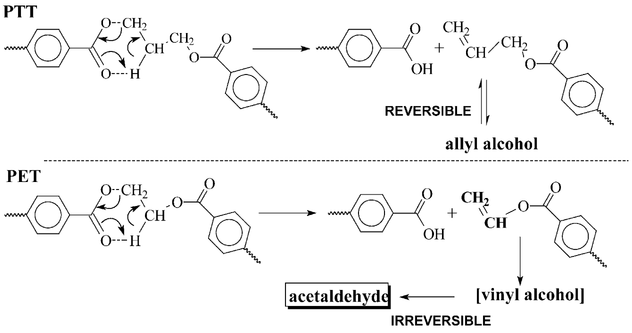
The thermal degradations of polyesters have been studied extensively under a variety of conditions [7], although fewer investigations of PET [9–17] and PBT [18–20] have focused on conditions pertinent to the polymerization reaction, i.e. at <300 °C under inert atmosphere. A common mechanism proposed for polyalkylene terephthalate degradations under these conditions is the electrocyclic, concerted oxo retro-ene reaction [7,10,19], a well-known thermal reaction of simple alkyl esters, such as ethyl acetate [21] (Schemes 1 and 2).

The stability of the allyl endgroups of PTT at 240–280 °C provides a convenient means to determine the decomposition rate by ^{1}H NMR and to compare the rates with the decrease in molecular weight by intrinsic viscosity (IV). Similarly, the degradation of PBT can be determined by measuring both butenyl endgroups and IV. To our knowledge, this is the first kinetic study of the thermal degradation of polyalkylene terephthalates determined by both NMR and IV methods.

Goodings [8], Zimmerman [10], and others have shown that reaction conditions, particularly mass transfer effects, can alter the apparent degradation rate due to competition from productive esterification reactions. In order to minimize productive reactions and oxidation, our samples were carefully degassed with N_2, held under 1 atm N_2 and were not stirred to minimize volatilization of glycol and/or water. This assured that the observed kinetics reflect the inherent thermal degradation as closely as possible with little or no contribution from competing propagation reactions.



Scheme 1. Comparison of catalyst effects on PTT and PET (adapted from Ref. [10]).



Scheme 2. Comparison of PTT and PET endgroup chemistry.

3.1. Rates and activation energies for PTT

The formation of allyl endgroups in PTT at 240–280 °C over 6 h is shown in Fig. 1. The first-order kinetic plots based on this data were highly linear (Fig. 2, Table 1). Because of slight curvature at 280 °C after 6 h, possibly due to slow loss of allyl alcohol, the rate at this temperature was calculated for the 4-h reaction time.

The decrease of PTT molecular weight measured by IV at the same temperatures is shown in Fig. 3. First-order kinetic rate constants (Fig. 4) were determined from Eq. (1) [13,19,20,22]:

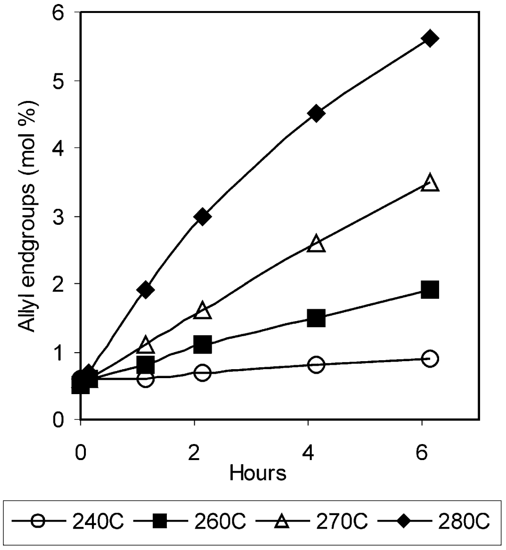


Fig. 1. Allyl endgroup formation in PTT at 240–280 °C by NMR.

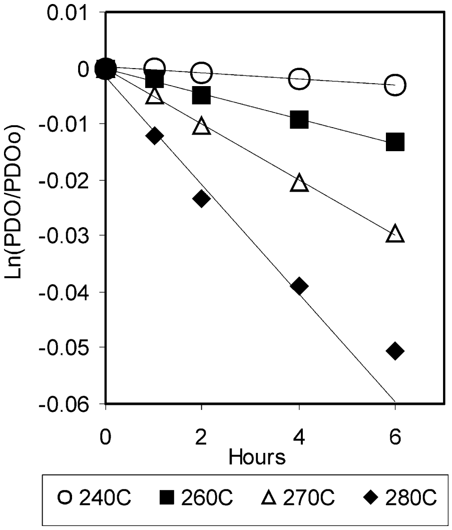


Fig. 2. First-order kinetics of PTT thermal degradation based on allyl endgroups.

$$\left(\frac{1}{\mathrm{DP}}\right)-\left(\frac{1}{\mathrm{DP}_0}\right)=kt \qquad (1)$$

where DP is the degree of polymerization and DP_0 is the initial value. The Mark-Houwink relationship determined for PTT [23]

$$\mathrm{IV}=K[M_\mathrm{w}]^a \quad K=0.00054 \quad a=0.69$$

was used to calculate DP assuming $M_\mathrm{w}/M_\mathrm{n}=2$ in the melt and $\mathrm{DP}=M_\mathrm{n}/206$, using the PDO–TPA repeat unit molecular weight in order to compare the allyl endgroup formation and IV decrease on an equal basis.

The rate constants k determined by allyl endgroups and by IV show excellent agreement within experimental error (Table 1), which supports the concerted, electrocyclic retro-ene reaction (Schemes 1 and 2) as the predominant or exclusive mechanism for random chain cleavage under these conditions. If other significant degradation mechanisms were occurring simultaneously, the rate constants for molecular weight degradation would necessarily be greater than the rate determined from the increase in endgroups.

The activation energies E_a determined from Arrhenius plots of ln(k) vs. 1/T K (Fig. 5, Table 1) also show excellent agreement between the two methods, averaging 168±8 kJ/mol (40±2 kcal/mol).

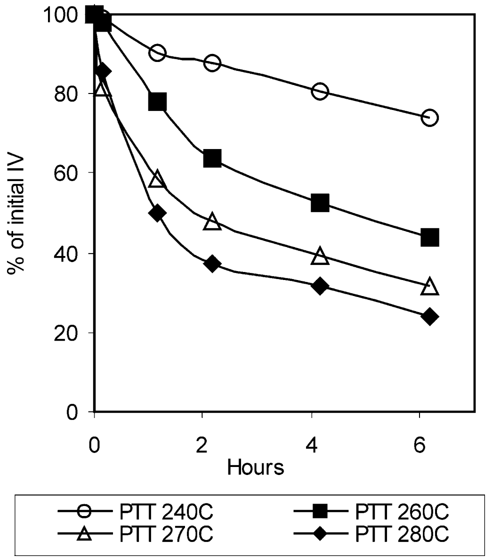


Fig. 3. Molecular weight change (%) of PTT at 240–280 °C ($\mathrm{IV}_0=0.92$).

3.2. Catalysts, additives and processes

The degradation rates of several PTT compositions were determined under our standard conditions at 270 °C (Section 2), which is in the upper range of the practical polymerization temperature window for PTT [5]. In general, catalysts, additives and polymerization processes had little or no effect on the thermal stability of PTT (Table 2):

(a) Even with extremely low or ‘no’ catalyst present (~3 ppm Ti compared to ~40–80 ppm normally present), the degradation rates were within experimental error of the rate for the control sample (Exp. 1 and 2). Because of inherent and random errors that can occur in separate experiments, the control and ‘no catalyst’ samples were also examined in side-by-side degradation reactions (Exp. 3 and 4) and the decrease in IVs were indistinguishable (Fig. 6).

Table 1
First-order rate constants k and activation energies E_a for PTT and PBT

T, °C	PTT				PBT			
	Allyl endgroups (NMR)		Molecular weight (IV)		Butenyl endgroups (NMR)		Molecular weight (IV)	
	$k\times10^3$ (h^{-1})	r^2	$k\times10^3$ (h^{-1})	r^2	$k\times10^3$ (h^{-1})	r^2	$k\times10^3$ (h^{-1})	r^2
240	0.5	0.975	0.7	0.988				
260	2.2	0.996	3.2	0.996	3.5	0.993	2.4	0.985
270	5.0	0.999	5.5	0.993	5.5	0.989	4.0	0.986
280	9.7	0.987	10.6	0.988	13.5	0.997	9.3	0.997
E_a (kJ/mol)	176	0.999	159	0.998	166	0.963	167	0.983
E_a (kcal/mol)	42.0		38.1		39.6		39.9	
ln (A) (s^{-1})	24.4		21.9		23.4		23.4	

r^2 = correlation coefficient for linear regression.

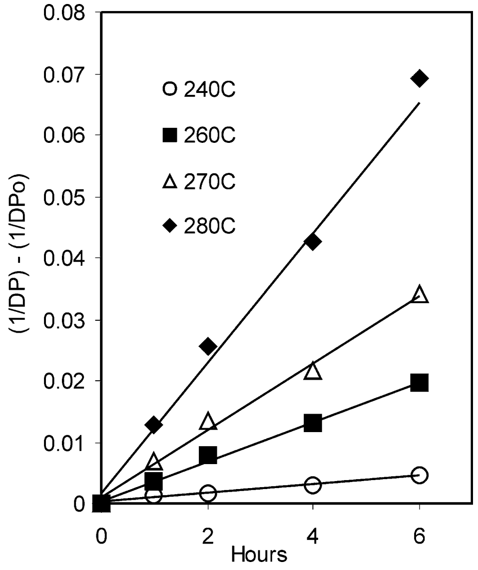


Fig. 4. First-order kinetics of PTT molecular weight degradation at 240–280 °C.

(b) Other catalysts, such as antimony, did not affect the degradation rate (Exp. 5–7).
(c) The degradation rates for high molecular weight PTT (IV ~ 0.92) prepared by all-melt processes [5] and by solid-state polymerization (SSP) [25] were the same (Exp. 6, 7, 11 vs. Exp. 1, 3, 10).
(d) Delustered polymer containing 0.4 wt% TiO_2 showed the same rate as clear polymer (Exp. 8 vs. Exp. 1, 3).
(e) Added cobalt acetate, a 'toner' used to improve color, did not affect the degradation rate (Exp. 9 vs. Exp. 1, 3).
(f) The level of dipropylene glycol comonomer (DPG; bis(3-hydroxypropyl ether)) did not affect the degradation rates based on allyl endgroup formation (Exp. 10–13). And limited IV data for these samples also showed consistent decreases during 1 h at 270 °C averaging 0.32 ± 0.02 IV units, which is within the estimated precision (Section 2). These results suggest that DPG ether units do not cleave significantly faster than PDO units under non-oxidative conditions, although the relatively low proportion of ether units in all of these samples limits the detection threshold if a separate mechanism were operative. Certainly there is no indication that PTT thermal stability was detectably improved for the compositions with lower DPG contents.
(g) PTT made using dimethyl terephthalate (DMT) rather than terephthalic acid (TPA) also did not exhibit any difference in degradation rates (Exp. 12, 13 vs. Exp. 6, 7, 11).
(h) Vacuum rather that nitrogen atmosphere slightly reduced the rate of molecular weight decrease of the high molecular weight control sample, but did not affect the rate of allyl endgroup formation (Exp. 15). A lower molecular weight PTT (IV = 0.64 dL/g) degraded at a slower apparent rate, based on both allyl endgroups and IV, under vacuum than under N_2 (Exp. 16 and 17) because of competing productive polymerization reactions promoted by removal of excess PDO and water.

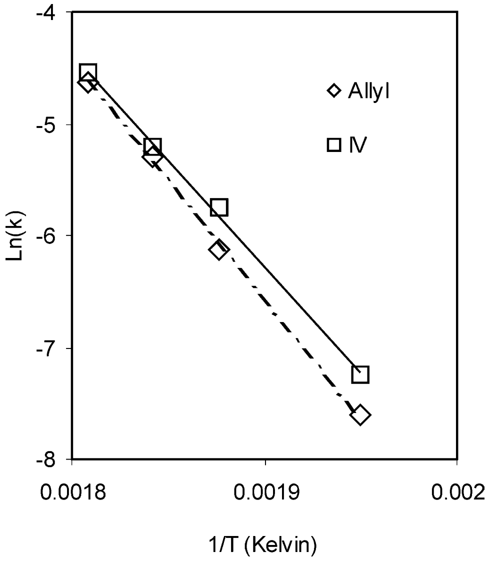


Fig. 5. Arrhenius plot for PTT thermal degradation at 240–280 °C.

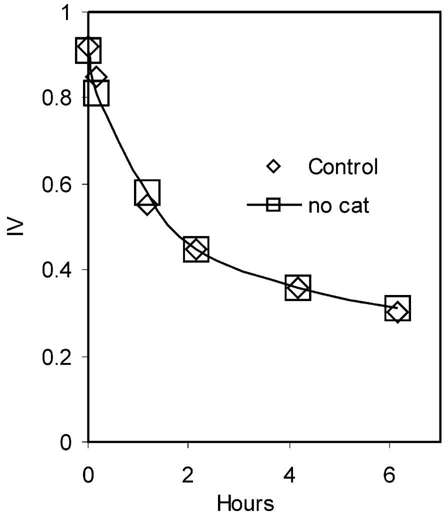


Fig. 6. Side-by-side comparison of 'no catalyst' PTT to control PTT.

The degradation of pure (>99.9%) PTT cyclic dimer was also determined by following the formation of allyl endgroups at 270 °C (Fig. 7). The rate (slope) was identical to the rate of the PTT control polymer (Table 2, Exp. 14). Because recrystallized cyclic dimer contains no metal catalyst or any other additives, these results support the conclusion that catalysts play virtually no role in PTT thermal degradation. However, catalysts may influence other PTT degradation reactions, such as hydrolysis or color formation.

Our results clearly demonstrate that the rate of PTT

Table 2
First-order rate constants k for various PTT compositions at 270 °C

Exp.	Composition	Process	$k \times 10^3$ (h^{-1}), NMR	r^2	$k \times 10^3$ (h^{-1} IV)	r^2
1	Ti catalyst (control)	SSP	5.0	0.999	5.5	0.993
2	'No catalyst' (3 ppm Ti)	SSP	4.3[a]	0.949	4.7	0.991
3[b]	Ti catalyst (control)	SSP	5.0	0.993	5.4	0.988
4[b]	'No catalyst' (3 ppm Ti)	SSP	4.1	0.989	5.1	0.986
5	Sb catalyst	SSP	4.5	0.957	5.1	0.987
6	Ti+Sb catalysts[c]	All-melt	5.7	0.969	5.5	0.957
7	Ti catalyst[c]	All-melt	4.8	0.998	4.7	0.990
8	TiO_2 0.4 wt%	SSP	4.8	0.981	5.2	0.988
9	Co toner	SSP	5.3[a]	0.992	5.7	0.987
10	DPG 3.0 mol%	SSP	5.2	0.996	[d]	
11	DPG 1.6 mol%	All-melt	5.2	0.977	[d]	
12	DPG 0.4 mol%	DMT	5.2	0.924	[d]	
13	DPG 0.2 mol%	DMT	4.9	0.943	[d]	
		Average	4.9±0.4		5.2±0.4	
14	PTT Cyclic dimer		4.8	0.981		
15	Control/vac[e]	SSP	4.9	0.994	4.6	0.992
16	Low IV[f]	All-melt	4.5	0.998	4.6	0.996
17	Low IV[f]/vac[e]	All-melt	3.7	0.981	3.5[a]	0.952

[a] Four-hour reaction time; all others 6 h.
[b] Side-by-side experiments.
[c] With 20 ppm Co toner.
[d] See Section 2.
[e] <2 mbar. r^2=correlation coefficient for linear regression.
[f] Initial IV 0.64 dL/g.

thermal degradation is not affected significantly by catalysts, additives or other process variables except temperature. In contrast, catalysts can influence the degradation of PET [10] and PET model compounds [9, 10], with titanium, zinc, and tin catalysts being more active compared to antimony or manganese catalysts. However, thermal degradation rates of PBT and PBT model compounds (e.g. 1,4-butanediol dibenzoate) have been reported to be unaffected by catalysts [10].

Zimmerman explained the difference between catalytic effects on PET and PBT degradation rates by the mechanism shown in Scheme 1, adapted here for PTT [10]. In the case of PET, a metal catalyst complexing to the adjacent ester carbonyl can affect the electronic distribution at the carbon involved in the electrocyclic hydrogen transfer. The electron withdrawing effect of the complexed metal can stabilize the transition state, lowering its energy and increasing the rate.

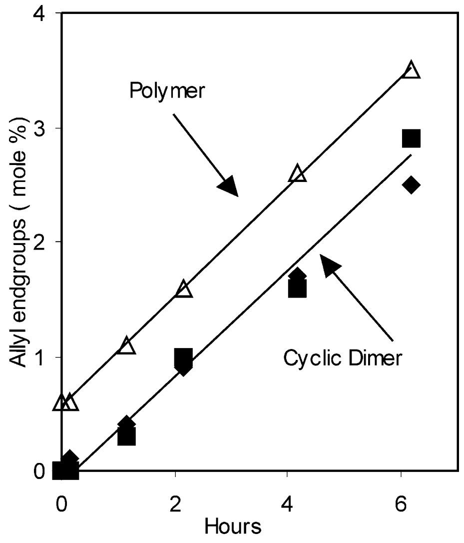


Fig. 7. Allyl endgroup formation by ^1H NMR for PTT cyclic dimer at 270 °C.

According to this mechanism, catalyst complexation at the adjacent ester groups of PTT and PBT cannot affect the retro-ene reaction because there is at least one extra, insulating methylene that prevents electron delocalization. This elegantly simple picture explains why PET degradation can be influenced by catalysts or additives and why PTT and PBT degradations are unaffected. Our results are entirely consistent with this mechanism.

3.3. Comparison to PBT

PBT forms the analogous butylene endgroups (–O–CH_2–CH_2–CH=CH_2) from retro-ene cleavage which also can be followed by NMR. The first-order kinetic rate constants k at 260–280 °C and calculated activation energy E_a for PTT were very similar to those of PTT (Table 1). Likewise, the relative molecular weight (IV) decrease for PBT was close to that of PTT. First-order kinetic analysis (Eq. (1)) based on Mark-Houwink constants [23] K=0.000070 and a=0.90 for IVs measured in hexafluoroisopropanol gave the rate constants and E_a shown in Table 1.

The first-order rate constants determined from both IV and butenyl endgroups for PBT are similar to previous reported values under similar reaction conditions.

Passalacqua and co-workers [18] reported $k = 12.4–13.3 \times 10^{-3}\,h^{-1}$ at 280 °C for samples under N_2, which agrees closely with our results of $9.3–13.5 \times 10^{-3}\,h^{-1}$. Van Bennekom and co-workers [20] reported $k = 1.9–2.2 \times 10^{-3}\,h^{-1}$ at 270 °C for samples stirred under N_2, which is somewhat lower than our $4.0–5.5 \times 10^{-3}\,h^{-1}$. However, stirring can increase mass transfer and allow competitive productive polymerization to proceed, lowering the apparent degradation rate.

3.4. Comparison to PET

In contrast to PTT and PBT, PET is significantly less sensitive to molecular weight degradation. At 270 °C, the IV of PET decreased <20% in 6 h compared to almost 60% decline for PTT (Fig. 8). The relative molecular weight decrease for PET at 290 °C was less than for PTT at 260 °C over the entire period in spite of the 30 °C temperature difference.

Even though PET appears to be more thermally stable than either PTT or PBT, the activation energies (E_a) for all three polymers are very similar. Table 3 summarizes pertinent literature values for E_a reported under reaction conditions similar to those used in our experiments, e.g. under inert atmosphere and at similar temperatures, along with the values we determined for PTT and PBT. Note that E_a based on melt viscosity (rheology) tends to be higher than measured by other methods. Even though E_a for PET can be influenced by catalysts and reaction conditions [8,10], most of the values hover around 160–175 kJ/mol (~38–42 kcal/mol) for all three polyesters.

The calculated activation energies for the retro-ene cleavage of model compounds for PET, PTT and PBT using PM3 semi-empirical calculations are within ~5 of 210 kJ/mol (Table 4). Although the calculated energies are higher than the experimental values for the polymers, the relatively small differences in E_a are consistent with the experimental observations that E_a's for the polyesters are similar, especially in the absence of catalyst or mass transfer effects.

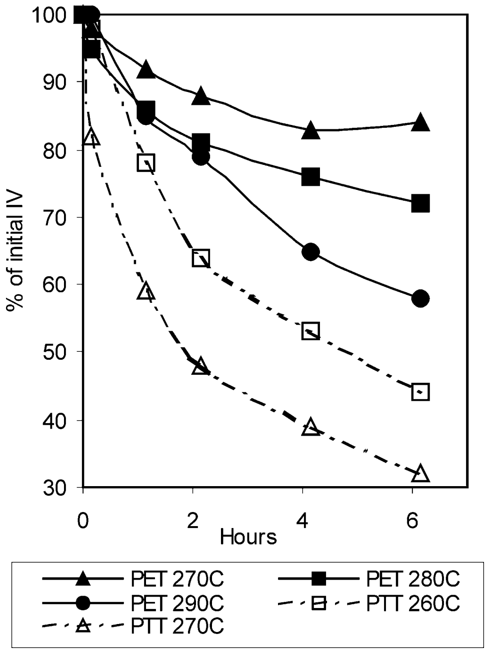


Fig. 8. Comparison of the degradation in molecular weight of PET at 270–290 °C to PTT degradation at 260–270 °C.

Table 3
Comparison of activation energies E_a for polyester thermal degradations

	E_a (kJ/mol)	Method	T (°C)	Ref.
PET	172	IV (ultrahigh M_w)	290–310	[16]
	159	IV	275–315	[13]
	159	TGA	280–320	[15]
	153–191[a]	COOH endgroup	280–300	[10]
	189	Rheology	260–290	[19]
	174–221	Rheology	280–300	[14]
PTT	176	NMR (allyl endgroup)	240–280	
	159	IV	240–280	
PBT	166	NMR (butenyl endgroup)	260–280	
	167	IV	260–280	
	162–168	COOH endgroup	250–280	[10]
	172	IV and COOH	240–280	[18]
	192	Rheology	243–267	[19]

[a] Catalyst dependent; 'closed' system.

Entropy could also influence the thermal cleavage rates of PTT or PBT [19] compared to PET. The calculated pre-exponential factors, ln(A), are $21.9–25.4\,s^{-1}$ for PTT and about $23.4\,s^{-1}$ for PBT (Table 1). By comparison, ln(A) for PET has been reported to be near 25 for 'closed' systems [10], in the range of 11–21 for 'open' systems [10], and as high as $27–32\,s^{-1}$ [15,19]. Although we cannot completely rule out an entropy effect on the difference in apparent thermal degradation rates of PTT (or PBT) and PET, it is also very difficult to make any quantitative comparisons for two reasons: (a) The extrapolated value of ln(A) is very sensitive to small differences or errors in the kinetic data and (b) the true value of ln(A) and the corresponding activation entropy for PET is difficult to determine accurately because the actual rate of chain cleavage of PET is masked by competing propagation reactions, as discussed below.

Table 4
Activation energies of retro-ene cleavage of model reactions by PM3 semi-empirical MO calculations

	E_a (kJ/mol)
EG dibenzoate	206[a]
PDO dibenzoate	206
BDO dibenzoate	213[b]
EG bis(methyl terephthalate)	213
PDO bis(methyl terephthalate)	205
BDO bis(methyl terephthalate)	214

[a] Exp. 174 J/mol [10].

[b] Exp. 171 kJ/mol [10].

Table 5
Comparison of thermal degradation factors for PTT and PET chain cleavage

	PTT	PET
Catalysts	No effect	Can influence rate[a]
Activation energy, E_a (kJ/mol)	160–175	150–190[a]
Endgroup stability	Stable	Unstable
Endgroup loss, calcd ΔG (kJ/mol)	-3	-67
Endgroup transesterification	Reversible	Irreversible
Conversion factor, $\Delta\mathbf{p}$	Decreases	Decreases
Stoichiometric ratio, $\Delta\mathbf{r}$	Unchanged	Increases → 1.0

[a] Based on literature references.

3.5. Endgroup chemistry

The apparent greater thermal stability of PET compared to PTT and PBT is proposed to be fundamentally related to the instability of vinyl endgroups formed during PET degradation, which contrasts with relatively stable, chain-terminating allyl and butenyl endgroups formed by chain cleavage of PTT and PBT, respectively, under the experimental conditions used here. This difference in endgroup stability provides a competing, compensating mechanism for PET [10] that is not available for PTT and PBT.

The critical differences in the endgroup chemistries for PET and PTT are summarized in Table 5 and Scheme 2. Vinyl endgroups formed by the retro-ene cleavage of PET are unstable and easily, irreversibly lost as acetaldehyde. In our experience, the vinyl endgroups are very hard to detect even in highly degraded PET (<0.05 mol% by NMR) because the vinyl groups escape as acetaldehyde [8,10,17], especially under favorable mass transfer conditions during polymerization. Measurement of evolved acetaldehyde is one means to measure the thermal degradation rate of PET [8,10,11]. The thermodynamics for conversion of the vinyl endgroup to acetaldehyde via transesterification is very favorable ($\Delta G = -67$ kJ/mol) based on PM3 semi-empirical calculations.

In contrast, the allyl and butenyl endgroups produced from PTT and from PBT, respectively, are stable and not easily lost, especially under the low mass transfer conditions of our experiments. If transesterification releases free allyl alcohol, it will likely react with another ester or carboxylic acid rather than escape from the PTT polymer melt. The PM3-based calculated thermodynamics for loss of allyl alcohol via transesterification is nearly neutral ($\Delta G = -3$ kJ/mol).

Vinyl, allyl and butenyl ester endgroups are all chain-terminating groups that limit molecular weight, but the loss of unstable vinyl groups is equivalent to removing excess glycol which leaves active COOH endgroups that can participate in productive reactions [10]. However, because allyl and butenyl endgroups are relatively stable, their formation does nothing to improve the equilibrium stoichiometry.

A more explicit analysis requires consideration of the fundamental equilibrium statistics for condensation polymers, as described [24] by Eq. (2):

$$\bar{X}_n = \frac{1+\mathbf{r}}{1+\mathbf{r}-2\mathbf{rp}} \tag{2}$$

where $\bar{X}_n$ is the number-average degree of polymerization in terms of number of ester units, $\mathbf{p}$ is the conversion (fraction of COOH reacted) and $\mathbf{r}$ is the stoichiometric ratio for PTT

$$\mathbf{r} = \frac{C}{P+2A}$$

and C is the number of COOH groups (reacted or not), P is the number of PDO hydroxyls (reacted or not) and A is the number of allyl hydroxyls. For PET, $\mathbf{r} = C/EG$ where EG is the number of glycol hydroxyls (reacted or not) and there is no corresponding endgroup in the denominator for PET because the vinyl endgroups are unstable.

To achieve high molecular weight, both $\mathbf{p}$ and $\mathbf{r}$ must be close to 1.0. As defined here, $\mathbf{r}$ is slightly less than 1.0 because polyesters are made using excess glycol, which persists in the final polymer. For example, typical PTT at IV $\sim$ 0.92 dL/g with 10 meq/kg COOH endgroups and 0.5 mol% allyl endgroups, contains approximately 60% PDO endgroups, 30% allyl endgroups and 10% COOH endgroups.

Each retro-ene chain cleavage of PTT produces one COOH and one allyl endgroup. Therefore, conversion $\mathbf{p}$ decreases, which requires the equilibrium molecular weight $\bar{X}_n$ to decrease unless subsequent productive reactions can occur. However, the stoichiometric ratio $\mathbf{r}$ is unchanged because the number of carboxyls C is not affected by chain cleavage, the PDO hydroxyls P have decreased by two for each cleavage because of transformation to the allyl endgroup, but the allyl hydroxyls A also increase by one. Because the allyl group is chain-terminating, it counts twice [24]. The net effect is that $\bar{X}_n$ decreases for PTT only because $\mathbf{p}$ has decreased.

In contrast, when PET chain cleavage occurs (Scheme 2), the unstable vinyl endgroup is lost via transesterification with an ethylene glycol endgroup or by hydrolysis. The cleavage reaction forms COOH endgroups and $\mathbf{p}$ decreases at least as much as for PTT. The irreversible loss of a vinyl endgroup as acetaldehyde removes two EG hydroxyls, so $\mathbf{r}$ increases closer to 1.0 because the polymer initially contains an excess of total hydroxyls in relation to total carboxylic acid units. The stoichiometric ratio $\mathbf{r}$ actually becomes more favorable for each PET thermal chain cleavage, which requires an increase in the equilibrium molecular weight $\bar{X}_n$ (Eq. (2)).

Therefore, the observed change in molecular weight for PET during thermal degradation is the net result of competing effects: One that decreases the molecular weight ($\Delta\mathbf{p}$) and one that increases the molecular weight ($\Delta\mathbf{r}$). For PTT and PBT, there is no compensating improvement in stoichiometry because $\Delta\mathbf{r} = 0$. From this point of view, the higher stability of PET is not necessarily because PET is inherently less susceptible to thermal chain cleavage but because the decrease in molecular weight of PET is automatically attenuated by competing productive reactions. For this reason, the molecular weight change for PET is also not necessarily a reliable measure of its inherent thermal stability.

Modeling exactly how the molecular weight of PET will respond to the changes in **p** and **r** is more complicated than outlined here because **p** can be affected by how much productive esterification also occurs simultaneously, which depends on mass transfer effects [10] and other chain-forming side reactions, such as anhydride formation [7,10]. However, this does not alter the central hypothesis that the underlying difference in the apparent thermal stability of PET and PTT (and PBT) is largely due to the difference in stability of the endgroups produced by the retro-ene cleavage reaction, particularly under polymerization or equilibrium conditions.

4. Conclusions

The thermal degradation rates of PTT and PBT at 240–280 °C under non-oxidative conditions have been shown to be essentially the same whether measured by the increase in allyl and butenyl groups (NMR) or by the decrease in molecular weight (IV). This provides evidence that random electrocyclic, concerted oxo retro-ene cleavage is the predominant mechanism for thermal degradations of PTT and PBT under these conditions.

Unlike PET, the thermal degradation of PTT is not influenced by catalysts, additives or the type of synthesis. Even PTT prepared with very low catalyst (‘no catalyst’) and pure PTT cyclic dimer both undergo thermal degradations at the same rates as standard polymer. In this respect, PTT is similar to PBT. The Zimmerman mechanism [10] provides a consistent explanation for why catalysts affect PET but not PTT or PBT.

PET is more thermally stable to molecular weight decline than either PTT or PBT. However, the activation energies E_a for PTT and PBT are in the range of 159–176 kJ/mol (38–42 kcal/mol), which is similar to the pertinent E_a values reported for PET. The similarity of the activation energies for all three polyesters, in the absence of catalyst effects, is also supported by semi-empirical MO calculations on model systems. So, differences in activation energies are unlikely to account for the greater thermal stability of PET.

We believe the thermal degradation chemistry of PET is a unique case for polyalkylene terephthalates. The instability of the vinyl endgroups in PET results in a net loss of glycol units, which improves the equilibrium stoichiometry during degradation. This provides a competing, productive mechanism that partially compensates for the decrease in conversion by chain cleavage. However, PTT and PBT behave normally because allyl and butenyl are relatively stable, chain-terminating endgroups and the overall stoichiometry does not change as a result of thermal chain cleavage. From this point of view, the inherent thermal stabilities of all three polyesters with regard to chain cleavage by the retro-ene mechanism are essentially the same, which is consistent with experimental and calculated activation energies.

Implications of our results for PTT polymerization processes are: (a) Reaction temperatures must be kept as low as practical, (b) reactive catalysts, such as titanium-based catalysts [5], are preferred in order to compensate for the low polymerization temperatures, and (c) additives or stabilizers will have little or no effect on the thermal degradation of PTT, although additives may influence other degradation reactions, such as oxidation. During processing into fiber, the lowest practical temperatures are desirable, as demonstrated by the successful commercial extrusion and spinning of PTT by several companies.

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